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13. ABSTRACT (Maximum 200 words) We have performed integrative studies of thermal and mechanical effects on the synthesis and properties of bulk titanium-based alloys with nanoscale morphological structures. Alloys are examined by calorimetry, mechanical-property testing, and x-ray and electron diffraction including high-resolution analytical microscopy. New titanium alloys with unusual structural and physical properties are found and preliminary studies of various phase formation pathways have begun, several key results are reported: (i) A series of high-order β -phase Ti-alloys obtained as ingots are found to undergo nanocrystallization and amorphization upon annealing. The premise for solid-state vitrification and nanocrystallization (SSVN) is studied in light of the free energy difference between the β phase and amorphous phase. (ii) The study of SSVN is generalized to include SSV via the mechanical pathway. The easy amorphization via mechanical milling is found to correlate strongly with SSVN via annealing, which provides the basis for future study of "inverse melting" in our Ti-alloys. (iii) Nanoscale spatial resolution of spinodal decomposition in high-order β Ti-alloys during isothermal annealing is studied using high resolution analytical electron microscopy. (iv) The study of SSVN has also resulted in a new class of high-strength β alloys with good ductility obtained in 85 at.% Ti-alloys with uniformly dispersed nanocrystalline α -phase particles.				
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Synthesis and Fundamental Studies of Bulk Metallic Systems Based on Unusual Microstructures

Statement of the problem studied

The objectives of our research are to synthesize bulk metallic alloys based on unusual microstructures down to the nanometer level, to carry out fundamental studies of their formation and thermal stability as well as their structural and physical properties, and to evaluate the technological potential of the new materials. Microstructures to be studied include those of glass and nanocrystal as well as glass-nanocrystal and nanocrystal-crystal composites. Structure-property relationships in the new alloys are also investigated.

Summary of the most important results (refs. to our publications are noted):

(1) Bulk titanium alloys with uniformly distributed nanoscale disordered regions^{P4}

We have found a series of titanium alloys that upon casting their ingots in an arc furnace or by air cooling the solutionized ingots of β alloys and subsequent annealing at 400-425C, partial amorphization and nanocrystallization occurred in conjunction with a phase transformation from β to β' . Over one hundred four-component and five-component Ti-based alloys containing Cr, Cu, Mn, and Fe were studied. The alloys typically contain 60-70 at.% Ti. Optimal alloy compositions for easy vitrification/nanocrystallization upon annealing were found to fall within a narrow range centered near $\text{Ti}_{65}\text{Cr}_{13}\text{Cu}_{16}\text{Mn}_4\text{Fe}_2$. Combining conventional and high resolution electron microscopy studies, it was inferred that amorphization started in high energy regions such as phase and grain boundaries. The premise for amorphization is the reduction of the free energy difference between an amorphous phase and a metastable crystalline phase (β in the present case) with proper alloys additions, and that this free energy difference is less than the excess energy associated with the high-energy regions. The alloys studied have provided a model system for studying the outstanding issue of bulk amorphization in the solid state, which is fundamentally different from amorphization of liquid alloys as in bulk metallic glasses. Since only air cooling was involved in the synthesis and processing, ingots could be produced for large-scale applications. An United States patent on our invention alloys has been awarded (see "Creative Products" below).

(2) Study of solid-state transformation of titanium alloys via mechanical alloying^{P3, P6}

We have also utilized mechanical milling (mechanical alloying) to make Ti-based amorphous alloys. This generalized study of solid-state amorphization allows the comparison of vitrification via thermal and mechanical pathways, known as thermodynamical melting and mechanical melting, respectively. Also interesting is that to date most studies of solid-state vitrification via mechanical milling of alloy powders have used ordered intermetallic compounds as starting materials instead of solid solution alloys. We found a strong dependence of critical

19981228 119

milling time, that is the minimum milling time required for complete amorphization, on alloy composition near those that could be amorphized via annealing (see (1) above). The formability of amorphous phase was found to improve significantly from the binary to the five-component alloys. The shortest critical time was found to be three hours, which was much shorter than for intermetallic compounds. Morphological structures obtained in both ingot and ball-milled samples were examined by electron microscopy, their stability was studied by calorimetry. The strong correlation of amorphization effects observed is consistent with the mechanism where the formation of amorphous regions in the annealed alloys is dependent on the free energy gap between the β phase and the amorphous phase, and how easily this gap can be closed. The smaller free energy gap of the solid solution, the less milling time that is required for complete amorphization.

(3) A new class of high-strength β Ti-alloys with good ductility^{P7, P8}

Our investigation of bulk amorphous/nanocrystalline Ti-based alloys over a wide composition range has also led to a new class of β alloys with uniformly dispersed nanocrystalline α -phase particulates in the β matrix. These alloys contain a high composition of 85 at.% Ti. The alloys were found to have a high strength of ~1650 MPa in comparison with typical strength of ~1000-1200 MPa for commercial Ti-alloys with comparable ductility. It is suggested that the mechanism of strength enhancement is similar to that found in aluminum glasses with nanocrystalline aluminum particles. A provisional patent #60-031,994 on these new β alloys has been granted, and in last November our University Patent Foundation had filed for patents both in the U.S. and abroad (see "Creative Products" below).

(4) Characterization of phase separation in some titanium alloys^{P5}

In our generalized study of nanoscale structure formation in novel titanium alloys, we have observed phase separation in some metastable β Ti-alloys during isothermal heat treatment at temperatures below 475C. During the early stages of the $\beta \rightarrow \beta + \beta'$ phase separation, the matrix was found to be in an extreme strained condition. Microstructural changes were monitored by high-resolution TEM and chemical profiles were studied by high resolution analytical TEM. It was observed that as the phase separation progressed, the composition gradient increased as the level of strain decreased. It was noted that, unlike other Ti-alloys reported, with copper as a nontraditional alloy addition, both bcc phases were still sufficiently stabilized after the completion of the phase separation to inhibit the formation of α , ω , and intermetallics. Distinct Cr rich and Cu rich regions in the coarsened nanostructure were revealed by chemical analysis. Our study has given the first real-space observation of nanoscale spinodal decomposition in an alloy, previous studies of spinodal decomposition utilized small-angle neutron scattering to obtain information in the reciprocal space.

Publications Resulting From ARO Contract No. DAAH04-94-0076

- P1.** Y.He, G.J.Shiflet, and S.J.Poon, "Ball milling-induced nanocrystal formation in aluminum based metallic glasses", *Acta Metall. Mater.* 43, 83 (1995).
- P2.** A.N.Mansour, C.A.Melendres, S.J.Poon, Y.He, and G.J.Shiflet, "A XANES study of the structure of passive films on amorphous *AlFeCe* alloys", *J. Electrochem. Soc.* 143, 614 (1996).
- P3.** D.J.Li, A.J.Akerman, K.J.Doherty, S.J.Poon, and G.J.Shiflet, "Swift amorphization of supersaturated titanium solution by mechanical milling", *Scripta Mater.* 38, 603 (1998).
- P4.** D.J.Li, K.J.Doherty, S.J.Poon, and G.J.Shiflet, "Bulk titanium-rich alloys containing nanoscale disordered regions", *Metallurgical and Materials Transactions* 28A, to appear.
- P5.** K.J.Doherty, D.J.Li, G.J.Shiflet, and S.J.Poon, "Characterization of the phase separation in a Ti-Cr-Mn-Cu-Fe alloy", to appear in Conference Proceedings of Materials Week'97 of the TMS-ASM International Joint Meeting, September, Indianapolis.
- P6.** D.J.Li, K.J.Doherty, S.J.Poon, and G.J.Shiflet, "Correlation of amorphization effects in titanium solid solutions via mechanical milling and annealing", submitted to *Phil.Mag.A*.
- P7.** D.J.Li, K.J.Doherty, G.J.Shiflet, and S.J.Poon, "A new class of β titanium alloys with high strength and good ductility", manuscript drafted, publication pending status of patent application.
- P8.** D.J.Li, K.J.Doherty, G.J.Shiflet, and S.J.Poon, "Structure-mechanical properties of high strength titanium alloys, manuscript drafted, publication pending status of patent application.

Creative Products

Awarded United States patent #5,626,691 "Synthesis and properties of bulk nanocrystalline titanium alloys", D.J.Li, S.J.Poon, and G.J.Shiflet.

Provisional United States patent #60-031,994 "A new class of high-strength β titanium alloys with good ductility", D.J.Li, K.J.Doherty, G.J.Shiflet, and S.J.Poon, applications for U.S. and foreign patents filed on Nov.21, 1997.

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